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New scenario for the accumulation and release of radiation damage in rock salt and related materials

H.W. den Hartog ^{a,*}, D.I. Vainshtein ^a, V.I. Dubinko ^{a,b}, A.A. Turkin ^{a,b}

^a *Solid State Physics Laboratory, University of Groningen, Nijenborgh 4, NL-9747 AG Groningen, The Netherlands*

^b *National Science Center, Kharkov Institute of Physics and Technology, 310108 Kharkov, Ukraine*

Abstract

Rock salt might be a promising geological medium for a radioactive waste repository. However, we have observed that even a basically stable compound such as NaCl may become unstable after heavy irradiation. As a result of the irradiation, dislocations, Na and Cl₂ precipitates and large voids are produced followed ultimately by sudden explosion-driven fracture of the material. We present a new concept of the radiation-induced micro-structural evolution, which explains the phenomena observed in heavily irradiated NaCl samples. This concept can be a prototype of a more general assessment of radiation effects in crystalline radwaste and repository materials, which is necessary for the evaluation of critical effects and maximization of the safety of repositories. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Formation of radiation damage in alkali halides and in particular, in NaCl, has attracted worldwide attention in the last two decades because of important geological applications related with nuclear waste management, e.g. the storage of high-level waste (HLW) in stable geological rock salt formations [1,2]. Rock salt can store energy of ionizing radiation emitted by HLW in the form of radiolytic products, i.e. colloidal sodium and molecular chlorine, which was the subject of numerous investigations [3–9], some of them concluding that saturation of radiation damage with increasing irradiation dose occurs well within the ac-

ceptable range for repository safety [6,7]. On the other hand, more recent systematic experiments on many heavily irradiated samples have shown that in many doped and natural rock salt samples, the stored energy value increases with increasing dose without any sign of saturation [8] and more important is that large voids are produced, which initiate explosive fracture of the samples [9].

In ionic crystals, generally, the numbers of displaced ions are different for different sublattice components, either because radiolytic displacements occur on a single sublattice (like in alkali halides or in fluorite) or because the target ion masses and displacement energies differ in simple binary collisions (like in Al₂O₃). So the formation of commonly observed stoichiometric defect aggregates (e.g. perfect dislocation loops and voids) requires secondary mechanisms for the formation of lacking components to preserve local stoichiometry. Until recently, the only known secondary

* Corresponding author. Tel.: +31-50-363-4178; fax: +31-50-363-4879.

E-mail address: h.w.den.hartog@phys.rug.nl (H.W. den Hartog).

mechanism was that proposed by Hobbs et al. [3] for halides to explain perfect loop formation in the absence of displacements in the cation sublattice. However, this mechanism cannot explain the simultaneous formation of voids, observed in many ionic systems [2,9].

The main purpose of this paper is to present our new results in one concise article and put forward a new scenario for the accumulation and release of radiation damage in rock salt and related materials. To do so we need to summarize shortly some of our relevant results obtained earlier, showing the very unusual behavior of heavily irradiated rock salt.

2. Void formation in irradiated NaCl

Experimental data [9] obtained for pure, doped and natural rock salt samples, which had been irradiated with 0.5 MeV electrons up to fluences of 6×10^{18} electrons/cm² (i.e. about 300 Grad), show that with increasing irradiation dose, voids are

formed followed by their transition to large (hundreds of nm in size) penny-shaped cracks resulting in a subsequent explosion-driven fracture of the material (Fig. 1). The latter violent effects have been studied extensively during carefully executed annealing experiments [10], but we have also found strong evidence that explosion-driven fracture occurs during irradiation at very high doses. Our earlier experimental results, which have been discussed at length in [10] demonstrate very clearly that the observed explosive phenomena are driven to a large extent by instantaneous back reactions between colloidal Na and Cl₂ precipitates and cannot be explained by catastrophic cracking, which has been observed in insulators during implantation.

The problem of void formation in ionic crystals is similar but more complex than that in metals. Indeed, it is possible to explain the transition of gas “bubbles” to voids above a critical number of gas atoms required for the onset of the bias-driven cavity growth (swelling) [11]. However, to do so in ionic crystals one needs a source of stoichiometric

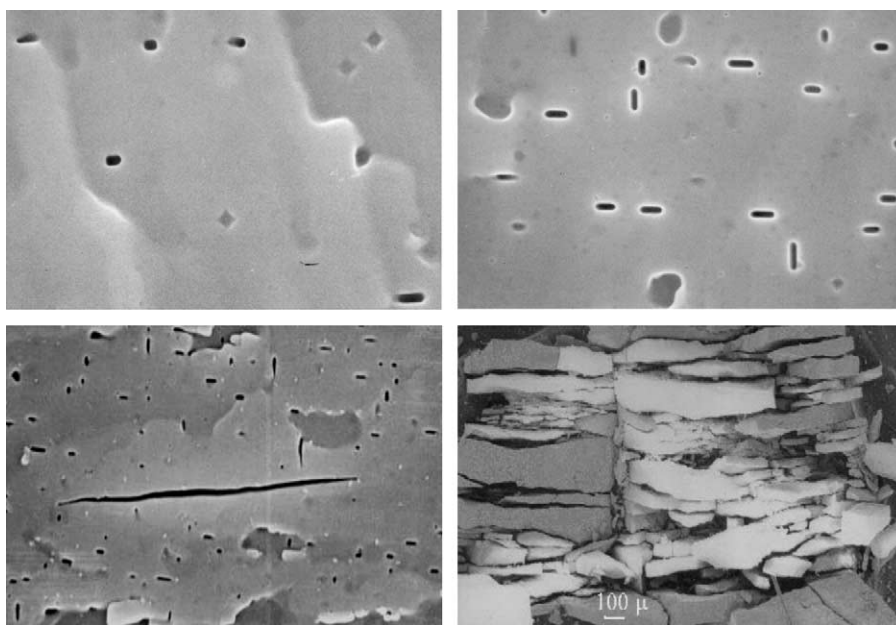


Fig. 1. SEM micrographs showing vacancy voids and cracks in natural rock salt crystals irradiated with 0.5 MeV electrons at 100 °C. (a) Equiaxial void at high resolution after irradiation to 60 Grad; LHM of metallic Na is 0.69 J/g; (b) “Penny-shaped” crack formed after irradiation to 300 Grad, LHM of metallic Na is 1.51 J/g; (c) Long crack formed after irradiation to 300 Grad, LHM of metallic Na is 2.5 J/g; (d) SEM micrograph of the exploded sample reveals large fragments and dust-like particles.

vacancy pairs that would provide the “free space” required for the bubble-to-void transition. The vacancy pairs formed during dislocation climb by the conventional mechanism [3–5] cannot be such a source since they are occupied by halogen molecules and essentially immobile. To explain void formation in alkali halides we have proposed an alternative mechanism of dislocation climb [12,13], which involves the production of cation vacancies as a result of the absorption of H centers at dislocation lines. Recombination of cation and anion vacancies results in the production of stoichio-

metric vacancy pairs and ultimately in void growth.

3. Explosive fracture of rock salt due to back reactions between radiolytic products

According to the present view, chlorine bubbles are the most finely dispersed extended defects in the system (Fig. 2) implying that rapidly growing voids start to collide with bubbles first, which would fill the voids with chlorine gas. One can

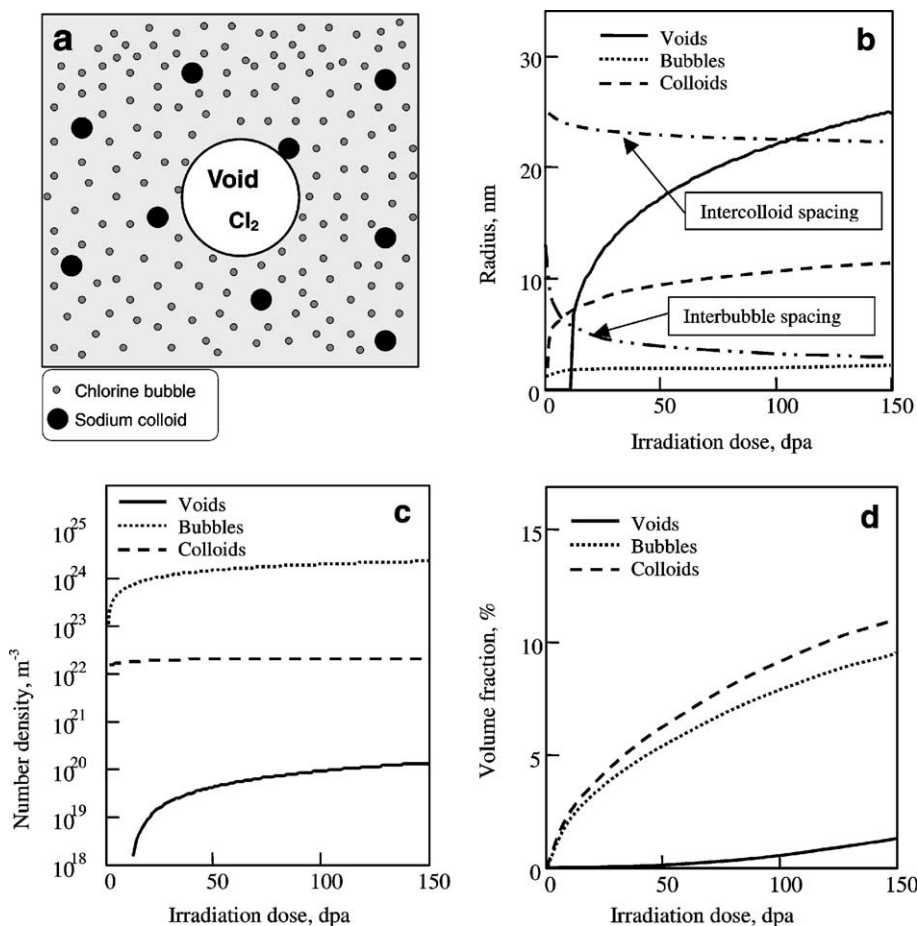


Fig. 2. Evolution of bubbles, colloids and voids with increasing irradiation dose (in displacements per anion, dpa) calculated for the laboratory irradiation conditions (100°C , 3×10^{-5} dpa/s) and a constant dislocation density 10^{14} m^{-2} [14]. (a) Graphic illustration; (b) Intersection between the colloid radius and interbubble spacing curves indicates a beginning of the explosive back reaction due to collisions between the bubbles and colloids resulting in the formation of voids, which grow to sizes exceeding the intercolloid spacing and thus provide for the following and larger step of the explosive back reaction; (c) and (d) show the corresponding number densities and volume fractions of radiolytic products.

estimate the gas pressure in voids to be about 5×10^{-3} GPa (50 atm), which is well below the surface tension of the voids [14]. However, the chlorine accumulation within the voids provides the “fuel” for the explosive back reaction with metallic sodium when growing voids start hitting colloids, which ultimately results in explosion-driven crack formation.

The amount of released energy in this reaction is proportional to (i) the energy released due to formation of one NaCl molecule and (ii) the number of molecules formed as a result of the collision. This results in a large and sudden temperature and pressure increase within the void and the surrounding salt (in the GPa range), which initiates crack propagation from the void along the matrix cleavage plane (100) if it is larger than some threshold value [15,16].

Fig. 1 shows the void-crack evolution in natural rock salt crystals with increasing irradiation dose and the corresponding amount of stored energy. The latter can be determined conveniently and non-destructively by measuring the intensity of endothermic latent heat of melting (LHM) peaks of metallic Na, which is proportional to the volume fraction of sodium colloids (and chlorine precipitates) produced by irradiation. It is seen that the crack length increases gradually, which can be explained by a combined mechanism of diffusion accumulation and explosive release of energy within the voids, by which the final crack length is determined by the rates of two competing processes, namely, the production and dissipation of heat. The heat production is determined by the rate of crack expansion in length and thickness resulting in the consumption of additional “fuel” (supplied by the chlorine and sodium precipitates). The heat dissipation is determined mainly by the rate of propagation of the temperature front, which is heated at the expense of the energy released in the back reaction, which reduces the gas pressure. The crack propagation stops as soon as the gas pressure falls below the threshold value. Accordingly, the final crack length is determined by the volume fraction and the number density of colloids, the crack propagation rate and other material parameters [15] (Fig. 3). At sufficiently large colloid volume fractions, the heat production

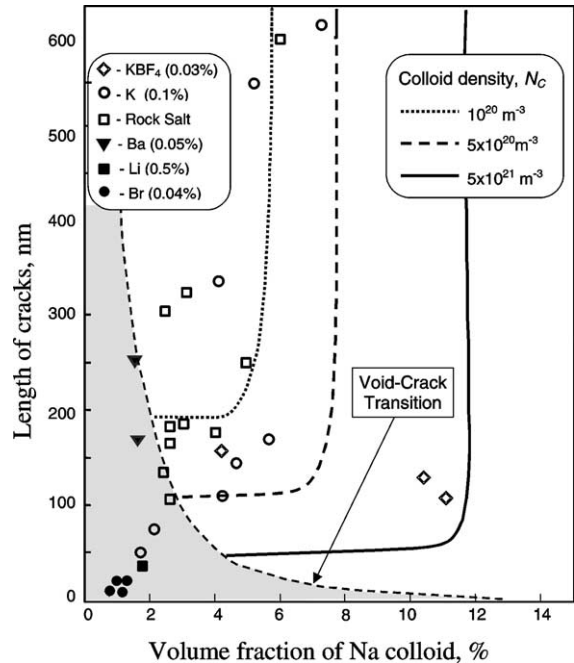


Fig. 3. Diagram showing the dependence of the maximum void size and the subsequent crack length on the colloid volume fraction, N_C [16]. Beyond a certain critical value (which depend on N_C), no stable crack exists, which implies that the positive feed back due to consumption of new “fuel” becomes stronger than the negative one due to the heat dissipation. Experimental points correspond to the maximum diameter of voids/cracks observed in materials with different dopants.

starts to dominate over its dissipation resulting in the unrestricted crack propagation and a subsequent explosive fracture of the material.

4. Summary and outstanding problems

We have presented a new scenario for the radiation-induced reactions between point defects and extended defects based on the present model. Primary radiation-induced point defects, namely, H and F centers, separate ultimately into bubbles, dislocations and metal colloids, which results in the production of secondary point defects (V_F centers) and extended defects (voids). The voids absorb fine chlorine bubbles during their growth and accumulate a large number of chlorine molecules before the collision with colloids starts, which changes the scale of the back reaction from the atomic to the macroscopic one.

We may conclude that a new concept of the radiation-induced micro-structural evolution in ionic crystals has been verified experimentally by phenomena observed in heavily damaged NaCl. The new concept can be a prototype of an adequate description of the long-term behavior of important insulating materials in intense radiation fields, which can be employed for an evaluation of the critical effects expected under conditions of storage of HLW and development of radiation resistant materials.

Acknowledgements

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